

SPECTRUM-PHENOMENA IN THE CHROMIUM COMPOUNDS.

BEING PART IV. OF THE SPECTRUM OF THE RUBY AND EMERALD.

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In Parts I to III of my investigation of precious stones published between 1909 and 1912 (Trans. Roy. Soc. S.A., I [2], p. 321, II [3], pp. 271 and 273, and II [4], p. 339), it was shown that the almost unique spectra of ruby and emerald are due to chromium oxide which has been compelled to vibrate in an abnormal or constrained manner, leading to the production of *narrow* absorption bands in the spectrum; the constraining substance in the case of the ruby is crystalline alumina, and in the case of emerald it is beryllium silicate. It was found, in support of this conclusion, that quite a moderate degree of heating abolishes the characteristic spectrum, leaving unaffected the "ordinary" spectrum of chromium. In other words, a hot ruby has much the same spectrum as a solution of chromium sulphate or chloride.

Further investigation has now been made to see if constrained vibration of ordinary chromium oxide could be induced by artificial means, so that the resulting mixture would show narrow absorption bands in the red in addition to the common broad band of unconstrained chromium (between the D and E lines in the case of violet salts and across D in the case of the green salts).

The only previously known cases of these narrow bands are those mentioned in Part II of this work, viz. (1) a hazy band at λ 6960 seen in K_3CrO_x , and (2) a very hazy band at λ 6800 in chromium borax and "microcosmic" beads and in CrA_3 solution.

The first attempt to make a "constrained" chromium solution was by use of concentrated sulphuric acid. This was successful, the solution showing a red transmission band bounded by two narrow absorption bands just as in the case of the ruby, although the bands are not in the same place. The simplest method of making this solution is to add a few *per cent.* of CrO_3 to concentrated sulphuric acid, heat, and gradually add small quantities of organic matter (*e.g.* starch) until the orange colour has

changed to deep green; it should then be sealed up to prevent absorption of moisture. The spectrum of this solution of $\text{Cr}(\text{HSO}_4)_3$ in H_2SO_4 shows a red transmission band going from λ 6880 to λ 6770, the position of the centre, which is not much affected by varying depth of colour, being at λ 6825. In very strong solutions, however, the two absorption bands bounding this transmission come closer together, and the transmission goes only from λ 6825 to λ 6780. The outer of the two absorption bands is very broad, going from about λ 7350 to λ 6880, and appears rather lighter at λ 7080, as if it really consists of two bands which coalesce in the centre. The inner absorption band is narrow, going from λ 6770 to λ 6660 with greatest intensity at λ 6730. The transmission band of the ruby spectrum is at about λ 6940, *i. e.* considerably further up the spectrum.

A second and even more striking example of the constrained chromium spectrum is obtained when glacial phosphoric acid is used instead of sulphuric acid. The product is a thick green syrup, which solidifies to a "glass" on cooling, and is a solution of $\text{Cr}(\text{PO}_3)_3$ in HPO_3 . Its spectrum shows a transmission band going from λ 6800 to λ 6705, centre λ 6755, very similar to that seen in the ruby, but about twice as broad when seen with an ordinary slit, and also much further down in the red. In this case the whole of the transmission is inside the B line of the solar spectrum, whereas in the H_2SO_4 solution the transmission touches the B line, and the ruby transmission is wholly beyond the B line. The outer absorption band has its centre at λ 6840 and extends from λ 6890 to λ 6800. The inner absorption band crosses the C line of the sun almost symmetrically, its centre being at λ 6590, and its range being from λ 6705 to λ 6480. There is also a third faint band with centre at about λ 6310. This band can also be seen in the emerald. It is probable that by adjusting the concentration of chromium in this medium (HPO_3) and so altering the depth of the absorption bands it would be possible to get a very close imitation of the emerald spectrum. The ruby spectrum, on the other hand, has not been reproduced except by means of alumina (*i. e.* in the artificial ruby); probably another weak acid (*e. g.* boric) would do if it could be induced to dissolve chromium oxide.

None of the other acids tried gave anything characteristic, *viz.* concentrated HCl , HNO_3 , HClO_4 , formic, acetic and citric acids, although a very faint hazy band at λ 6800 was seen in several of these solutions. Most of these comparatively anhydrous solutions have beautiful blue or violet shades, and change to bluish green on boiling.